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Microscale Zeta Potential Evaluations Using Streaming Current Measurements

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Abstract

We present a method for determination of zeta potential in capillaries and microscale devices. The use of streaming current measurements under pressure eliminates the need for high voltage measurements while providing a relatively simple means of approximating the zeta potential. This technique finds application in evaluation of coatings as well as materials for separations media and electrokinetic pumping. We will discuss the theory, in which sample porosity and tortuosity information are not required, and we will present zeta potentials of some organic and inorganic media.

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Microscale Zeta Potential Evaluation Using Streaming Current Measurements

Introduction

Materials such as silica beads and acrylate-based polymers containing charged surface groups are commonly used as chromatographic media in capillary electrochromatography (CEC) because of their ability to generate flow under applied potential and separate analytes by size and charge.¹ Higher surface charge density yields faster flow rates and thus lower separations efficiency. This phenomenon has led to considerable research to tailor separations media by modification of surface charge groups. More recently, these materials have been identified for use in microfluidic devices such as hydraulic pumps and actuators.^{2,3}

The ability of these materials to efficiently generate flow and cause separations or pumping is dependent upon the nature of the functional group as well as the size and porosity of the materials. One value that effectively combines these parameters is the zeta potential, which is the average potential at the surface of shear (see below). The zeta potential (ζ) is used to characterize the outer, diffuse part of the double layer; as such, it is useful for evaluating the interaction between a packed bed and the flow of liquid through it.⁴ A method of approximating ζ would be extremely useful in predicting efficiencies of chromatographic and pumping media. Unfortunately, ζ has proven difficult to determine in porous media, due to difficulties in obtaining sample porosity, restrictive factor, and tortuosity.¹

In cases where it is possible to determine porosity, tortuosity, and restrictive factor of porous plugs, ζ can be approximated using either streaming potential or streaming current measurements. In both cases, pressure is applied across the capillary; the resulting streaming potential and/or streaming current can then be

measured. Traditionally, streaming potential has been the method of choice^{5,6,7,8,9,10,11} because it avoids problems associated with electrode polarization.¹² However, electrode polarization can be avoided through the use of low concentrations of electrolyte (see below), and in fact streaming current measurements are fairly commonplace for large porous plugs.^{13,14} Streaming current measurements have the added advantage that, unlike in streaming potential measurements, surface conduction effects are negligible.⁴

Theory

The Debye layer is a thin, net-charged layer of ions which forms in order to shield charged sites on a solid surface. Although the details of the structure of the Debye layer have been debated since at least the early 1800's, it is generally agreed that at least a portion of the Debye layer is diffuse and mobile. Since the Debye layer represents a net charge density, convective (e.g., pressure-driven) transport of fluid within the mobile portion generates a net current known as streaming current. This phenomenon serves as the basis for measuring the electroosmotic mobility of a fluid in contact with a simple planar surface. Furthermore, in order to distinguish surface properties from fluid properties, the "zeta" potential, ζ , can be separated from the fluid permittivity ϵ and dynamic viscosity η , which also determine the electroosmotic mobility of the fluid $v_{eo} = \epsilon\zeta/\eta$. While there are many potential complicating factors to disrupt this simple view (such as nonlinear viscosity, or non-planar surface topology), much previous work has shown very good agreement when comparing the electroosmotic mobility determined using streaming methods, and determined by directly observing electroosmotic flow (EOF) in an electric field.

Streaming methods have several advantages over EOF measurements: they are generally faster, are less intrusive because they avoid the injection of dye into the system, and they avoid concerns of electrolytic modification of the solvent at the electrodes. For the present work we have chosen to use streaming current measurements to determine ζ (or, more exactly, the ζ inferred from the

electroosmotic mobility). This eliminates the need to account for the contribution of surface conductance in the Schmolduchowski equation for streaming potential; since the size of pores is small enough that this contribution (due to excess charge in the Debye layer) can be dominant.

In the simplest case of an open capillary, streaming current can be used to determine the zeta potential according to¹²:

$$I_s = \frac{\varepsilon \zeta \Delta P}{\eta l} A \quad \text{Equation 1}$$

where I is the streaming current, ε_0 is the permittivity of a vacuum, ε is the dielectric constant of the medium, A is the cross-sectional area, ζ is the zeta potential, ΔP is the pressure drop across the sample, and l is the capillary length. In a capillary packed with a porous medium, however, the theory is not as straightforward. Recent progress towards a comprehensive one-dimensional model has been reported by Paul et al.¹⁵ To summarize, their model predicts that the apparent current density (based on capillary cross-sectional area), I/A , is given by

$$\frac{I}{A} = \left(\sigma_{app} \frac{\Delta V}{l} - v_{app} \frac{\Delta P}{l} \right) F^{-1} \quad \text{Equation 2}$$

There are two contributions to the current: conduction due to an applied or generated E-field, and pressure-driven transport of net-charged species in the double layer. We note, however, the need to use an apparent conductivity, σ_{app} , in order to account for surface conduction – when pores are smaller than a few hundred nanometers, surface conduction (in the excess-charged double-layers) can dominate the apparent conductivity. Likewise, it is necessary to use an apparent electroosmotic mobility, v_{app} , in order to account for the thickness of double layers compared to the pores. F is called the “formation factor”, which

accounts for the geometrical restriction of E-field lines. F is unity for an open capillary, and larger than unity for a packed capillary. Hence in an open capillary, where double layers are thin, for the streaming current is recovered by setting $\Delta V = 0$, and $F = 1$. The formation factor is equivalent to the ratio of tortuosity/(constrictive factor \times porosity).¹

Neglecting any contribution due to surface conductance in σ it can be shown¹ that $F = R_{\text{packed}}/R_{\text{open}}$. Hence formation factor can be viewed as the ratio of packed capillary resistance to open capillary resistance, in the absence of surface conduction. This is difficult to achieve in practice for the materials studied here, where pore sizes are as small as a few hundreds of nanometers. Since the double layer is approximately 9nm thick in 1mM KCl, and has a conductance which is several times that of the bulk fluid, Paul et al. found that σ_{app} can be 2-3 times as large as the bulk conductivity. However, the double layer thickness is roughly proportional to the square root of the ionic concentration; hence the double layers can be made much thinner in 50mM KCl, at which point it is as thin as the site-to-site spacing of charge sites on the solid surface. Hence measurements of F are obtained by measuring the capillary resistance when filled with 50mM KCl, and comparing it to the calculated open capillary resistance using $\sigma = \sigma_{\text{bulk}}$ (a few representative measurements confirmed the accuracy of the calculated values).

Having obtained a reasonably accurate measurement of F in a high conductivity solution, streaming current measurements can then be obtained in lower conductivity solution (see below), and the apparent zeta potential can be calculated with the slope dI_s/dP :

$$\zeta = \left(\frac{dI_s}{dP} \right) \left(\frac{l\eta F}{\epsilon_o \epsilon A} \right) \text{ Equation 3}$$

Of practical importance during streaming current measurements is the avoidance of electrode polarization. We have assumed that $\Delta V = 0$ in Equation 3; however,

it turns out that only a few hundred millivolts of polarization can be a significant contributor of error, especially if the capillary resistance is not large. To illustrate this effect, consider that typical streaming currents through a 50 μm diameter capillary are on the order of tens of nanoamperes. In order to pass this current through small area platinum-wire electrodes, a polarization potential of a few hundred millivolts may be present across the electrodes, as illustrated in Figure 1. The Butler-Vollmer equation tells us that the polarization potential is a logarithmic function of the current density, resulting in the representation of the electrodes as diodes in the equivalent circuit shown in Figure 1. Hence, until the polarization voltage nears the equilibrium potential for the electron-transfer reactions, the back-conduction through the capillary can lead to nonlinear dependence of measured I_s on P applied, if the capillary resistance is not large enough.

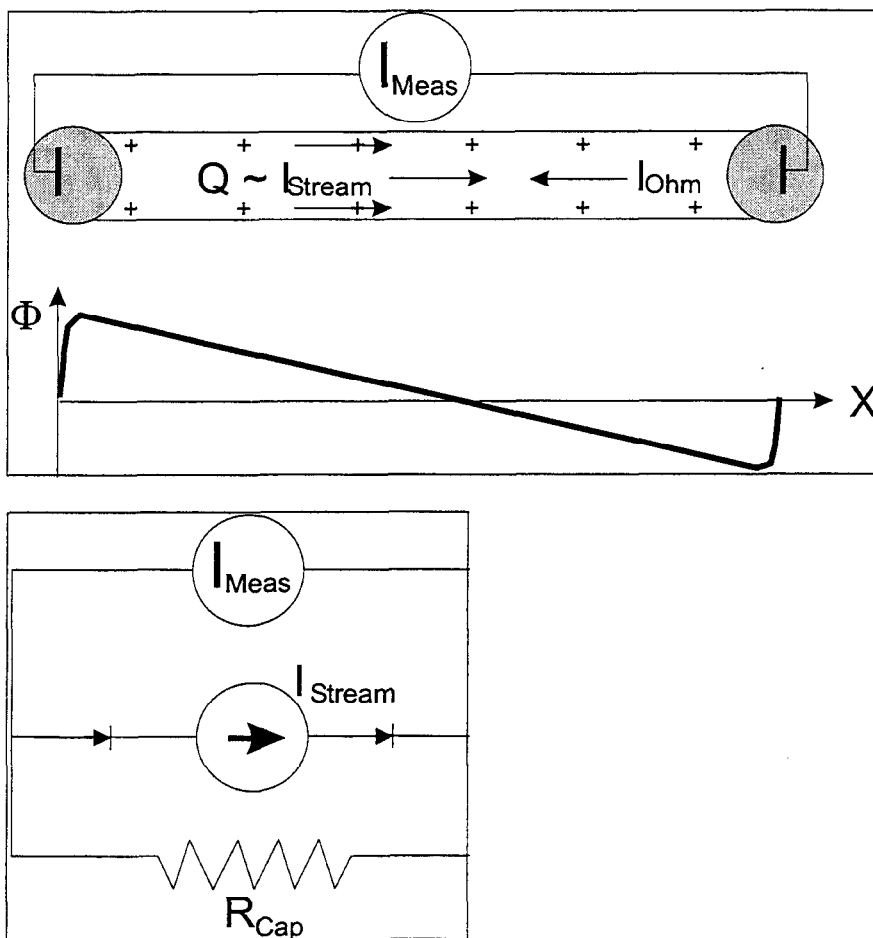


Figure 1: (a) System schematic (aspect ratio distorted for clarity). (b) Electric field potential profile through capillary and near electrodes, showing polarization. (c) Model circuit – diodes represent polarization at electrodes due to activation polarization.

A simple model describes some of the observable effects. Major assumptions are a one-step irreversible global hydrolysis reaction across the two electrodes,



with kinetics-limited polarization, absence of product, and symmetry factor $\alpha = 1/2$. In this case, the Butler-Vollmer equation describes the polarization of the electrodes, and the measured current can be calculated using Kirchoff's Law. The polarization voltage V_{pol} is the solution of the transcendental equation

$$I_s = i_{ex} A_{elec} \exp\left(\frac{V_{pol} - E_o}{RTnF\alpha}\right) - \frac{V_{pol}}{R_{cap}} \quad \text{Equation 5}$$

where A_{elec} is the electrode area, R_{cap} is the capillary resistance (a function of solution conductivity), and i_{ex} is the exchange current density of the reaction. This found, the measured current is the first term on the RHS of the equation, while the actual streaming current generated is the LHS of the equation.

For example, we have calculated the effect of electrode polarization in streaming-current measurements, assuming 50 μm diameter, 10cm long open capillaries, with $\zeta = 75\text{mV}$, and using KCl in water as the electrolyte. Exchange current density was assumed to be 1 mA/cm², although the results are fairly insensitive to this value. Calculated curves of I_s vs ΔP are shown in Figure 2 for various values of σ . The curves are nonlinear at low pressures because of the low source current provided, and the logarithmic dependence of the polarization voltage. Figure 3 shows experimental data for two cases with high and low conductivity, showing general agreement with predicted curves

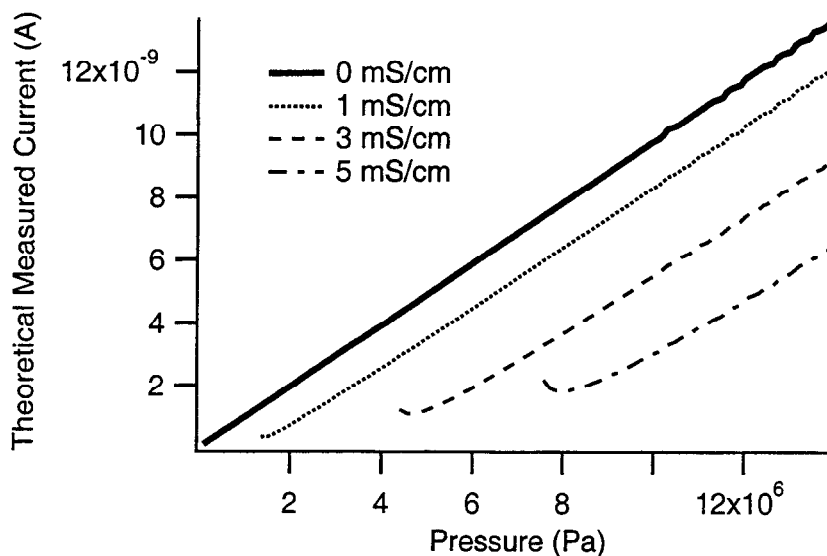


Figure 2: Theoretically calculated curves of measured (dashed) versus actual streaming current (solid) for a 10 cm long, 50 μ m ID capillary filled with solutions of conductivities 1 mS cm^{-1} , 3 mS cm^{-1} , and 5 mS cm^{-1} (left – right).

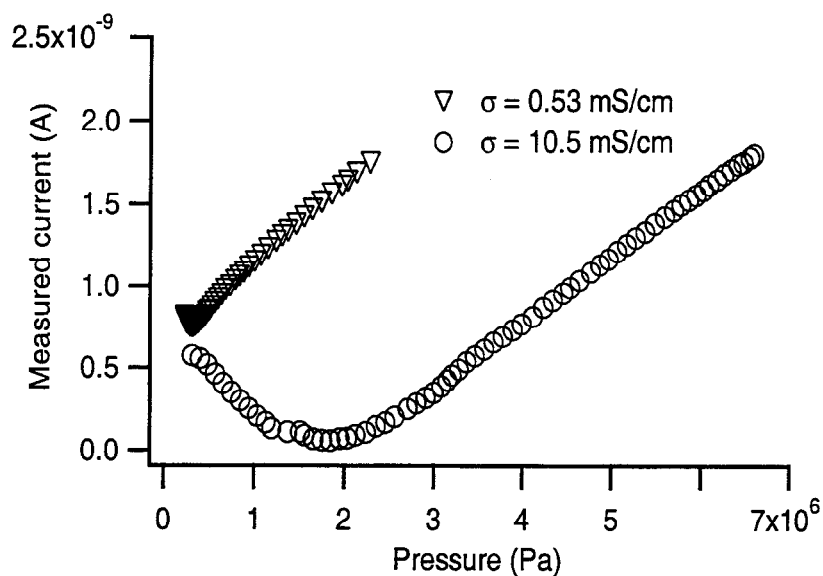


Figure 3: Experimentally determined streaming current dependence on applied pressure with solutions of 0.53 mS cm^{-1} and 10.5 mS cm^{-1} .

Experimental

Reagents

Reagent grade organic solvents such as ethanol were purchased from Aldrich and used as received. Potassium chloride and acetonitrile were purchased from Aldrich Chemical; acetonitrile was obtained in Sure/Seal™ bottles in an attempt to more accurately control water concentration in the buffer solutions. Porous silica particles were obtained from Phenomenex (Torrance, CA), and nonporous silica particles were obtained from EICHrom Industries (Darien, IL). Acrylate monomers were obtained from Aldrich and filtered through freshly activated alumina to remove inhibitor. The adhesion promoter z-6030 was obtained from Dow Corning and used without further purification. 2-Acrylamido-2-methyl-1-propanesulphonic acid (AMPS) and 2,2'-azobisisobutyronitrile (AIBN) were obtained from Aldrich and used as received. Glacial acetic acid was obtained from Mallinckrodt. Buffers were prepared using ~18 MΩ deionized water filtered through a Barnstead Nanopure II system (Dubuque, IA) and buffer salts were obtained from Sigma.

Procedure

Capillaries are packed with a variety of substrates. Monolithic polymers were prepared according to a procedure described elsewhere.¹⁶ The monomer was composed of 30% 1,3-butanediol diacrylate (BDDA) as the crosslinker, 0.3% z-6030 as an adhesion promoter, 0.5% AMPS to support electroosmotic flow, and 69.2% of a mix of monomers of varying hydrophobicity (Figure 7). In this study, the mix of monomers consisted of 59.2% n-butyl acrylate and 10% of the corresponding acrylate monomer listed in Table 1. The AIBN initiator was added at 0.5 wt% and the casting solvent was composed of EtOH (20%), MeCN (60%) and 5 mM phosphate buffer pH 6.8 (20%).

Silica-based particles are packed by sonication against a fused silica frit. Prior to streaming current measurements, capillaries are repeatedly rinsed with buffer

solution and held at constant pressure while monitoring streaming current until no further change in streaming current is seen; this indicated that the buffer is completely flushed and that the packing material is stationary and not compacting under pressure.

Apparatus

The microscale apparatus we have designed (Figure 4) to measure streaming current is similar to one used to determine streaming currents of much larger porous plugs.¹³ In our apparatus a buffer solution (5mM TRIS in 80:20 acetonitrile:water) is pumped into our capillary using a Jasco (Easton, MD) Model PU-980 HPLC pump. Pressure is monitored both with the pump's internal pressure transducer and an external transducer Model SP70 from Senso-Metrics (Simi Valley, CA) in-line between the pump and the capillary; an additional pressure transducer can be incorporated after the capillary in cases where there is not a complete drop in pressure across the capillary. The transducers are monitored with the use of a National Instruments DAQCard-1200 interface to a Powerbook G3 running Labview. The capillary is electrically isolated from other electronics by incorporating PEEK tubing between the capillary and other components and by enclosing the capillary and connectors in a Faraday cage. Both ends of the capillary are connected to PEEK tubing with Upchurch MicroTight Tee connectors, with platinum wire electrodes inserted into the tees. The platinum wires are connected to a current-to-frequency converter (Analog Technology Corp. Series 170, Duarte, CA), which exports data to a Hewlett-Packard 5316A Universal Counter. The counter interfaces to the computer through a National Instruments PCMCIA-GPIB card. Current is converted immediately to frequency because the frequency counter is much more sensitive to small changes in current; we have found that streaming currents obtained in this way are much more accurate than those determined using a Keithly 616 Digital Electrometer (Cleveland, OH). The Labview program yields streaming current data as a function of applied pressure, i.e. dI_s/dP in Equation 3.

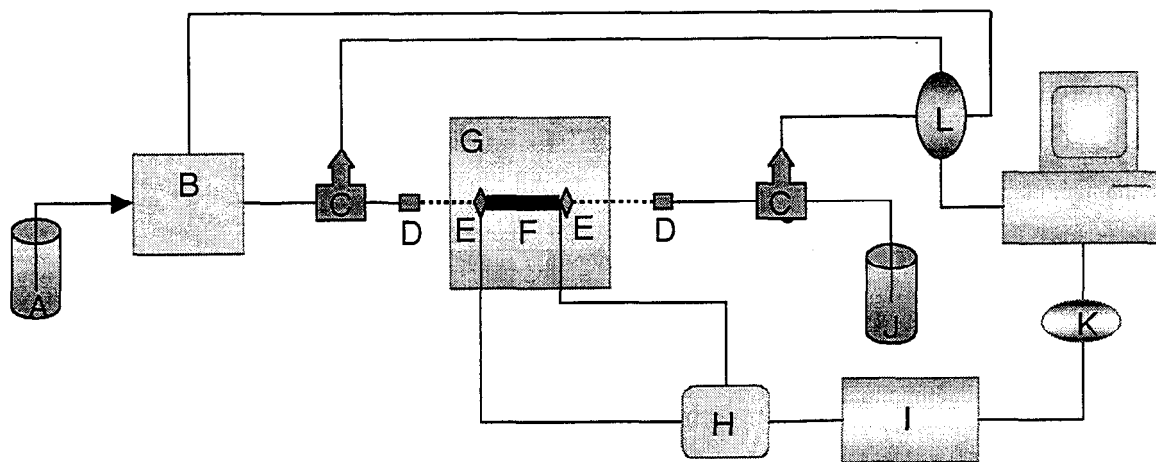


Figure 4: Apparatus used for streaming current measurements. A) Eluent reservoir, B) LC pump, C) Pressure transducer, D) Upchurch union, E) Upchurch MicroTee with platinum wire electrode, F) Capillary, empty or packed, G) Faraday cage, H) Current-to-frequency converter, I) Frequency counter, J) Waste eluent, K) GPIB interface, L) DAQCard-1200 interface.

Resistance across buffer-filled packed capillaries is measured using a Hewlett-Packard 4339B High Resistance Meter. Solution conductivities are measured using a Corning Model CD-55 conductivity meter. Solution dielectric constant and viscosity are approximated according to literature values;¹⁷ representative values of dielectric constants were validated in our laboratories using permittivity measurements from a Solartron 1260 Impedance Analyzer (Houston, TX).

Results and Discussion

Validity of Measurements

As a primary test of the validity of these measurements, the functionality of the current-to-frequency converter was confirmed. A series of potentials was applied across a resistor using a Constant Voltage Source (Model 5204, Electronic Development Corp.); frequency was measured at each potential and converted to current. Current and resistance were then used to confirm that the applied

voltage agreed with the calculated voltage (Figure 5). Pressure values were validated by comparing internal and external pressure transducer readings during each experiment. To examine the validity of Equation 3, we determined the zeta potential of non-porous silica using streaming current measurements. The value we obtained, -46mV, is within 10% of a typical literature value¹⁸ of -42mV. With the knowledge that the equipment and theory are both working, we are able to use this method to evaluate a variety of materials.

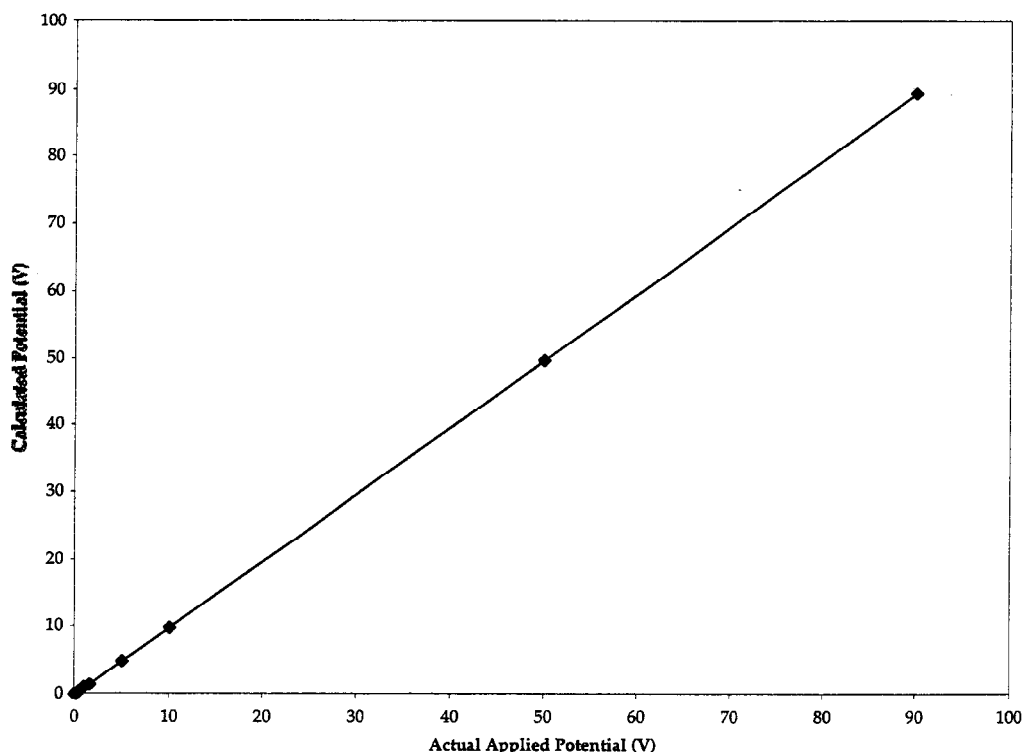


Figure 5: Validation of method using constant voltage source.

Because of the strong correlation of buffer composition to zeta potential, all packing materials were studied in the same buffer, a 5mM solution of TRIS in 80:20 acetonitrile water. This combination was chosen for compatibility with separations experiments being conducted within our laboratory;¹⁹ we have found that highest electroosmotic flow velocities (EOFs) are obtained when an high acetonitrile water ratio is used, this observation has been noted elsewhere.^{20,21} Both solvents exhibit favorable η/ϵ ratios, but the ratio is more favorable in water than acetonitrile. The positive effect on EOF with increasing acetonitrile

content has been attributed to increasing double layer thickness. We have also investigated the effect of increasing buffer conductivity on zeta potential. To this end, we have evaluated zeta potentials for a single packed capillary (porous polymer monolith with R=n-butyl) using the buffer described above with the addition of 0, 25, and 50mM KCl. Both streaming current and formation factor measurements were conducted in each of these buffer solutions, and zeta potentials were calculated. As can be seen in Figure 6, as [KCl] increases, the magnitude of the zeta potential decreases.

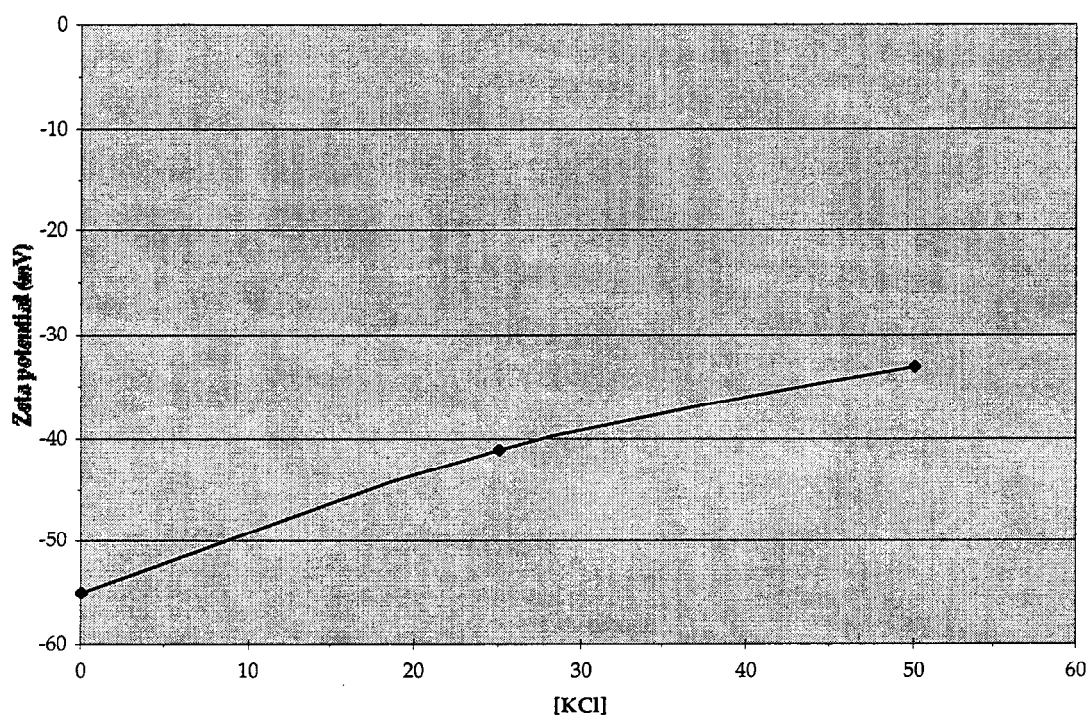


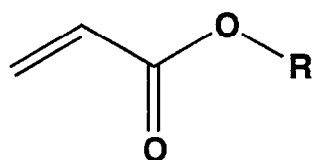
Figure 6: Effect of [KCl] on zeta potential.

Porous Polymer Monoliths

Acrylate-based polymers have recently become the focus of considerable interest for their use as separations media for capillary electrophoresis/electrochromatography. These materials are advantageous for their ease of positioning, since a monomer solution can be pumped into position and cured in place in a capillary or chip. No frits are necessary to hold the polymer in place, because an adhesion-promoting monomer (Figure 7) is incorporated to covalently bond the polymer to the substrate. Small changes in formulation often result in significant changes in EOF, dramatically changing separation properties.¹⁶ A series of acrylate-based monoliths has been prepared in our laboratories for use in separations and electrokinetic pumping application.¹⁶ Zeta potentials for these materials have been determined by using the streaming current method. It is important to note that Equation 3, which is used to determine ζ , assumes a lack of nanopores in the packing medium. While this assumption certainly holds true for the nonporous silica particles described above, the existence of nanopores in the acrylate-based monoliths has been suggested. If nanopores are present in the monoliths, the error this would propagate in the zeta potentials approximated here should be consistent across the series of monoliths we have investigated. However, while it is possible to compare zeta potentials within the acrylate series, it would be ill advised to compare those zeta potentials with those of non-nanoporous materials.

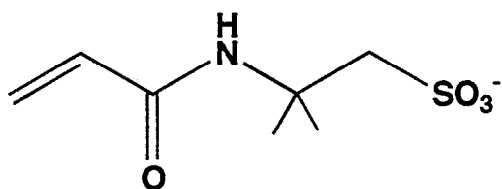
Table 1: Zeta potentials for a series of porous polymer monoliths

Functional Group	Zeta (mV)
ethyl	-116
n-butyl	-79
hexyl	-77
dodecyl Figure 2	-60
t-butyl	-40
THF	-38
ethylene glycol phenyl ether	-36

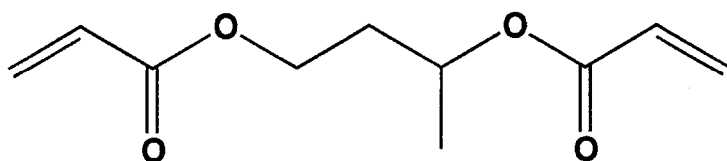


R = ethyl, n-butyl, t-butyl, etc

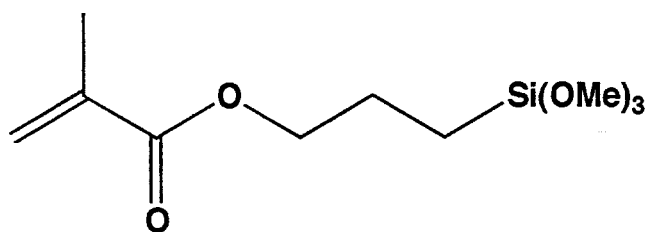
hydrophobic monomer



**charged monomer
(AMPS)**



**crosslinker
(BDMA)**



**adhesion promoter
(z-6030)**

Figure 7: Components of acrylate polymerization.

To examine the morphology of the acrylate-based polymer monoliths, we have applied significant pressure to force the monolith out of the substrate. Pressure requirements vary with polymer formulation, but we have found that the adhesion of the monoliths to the wall is stable to at least 2000psi, above which the polymer may be forced out of the substrate. For this reason, we ramp pressure to *ca.* 1300psi during streaming current measurements. The exposed monolith resulting from over-pressurizing the capillary can then be examined using SEM (Figure 8.)

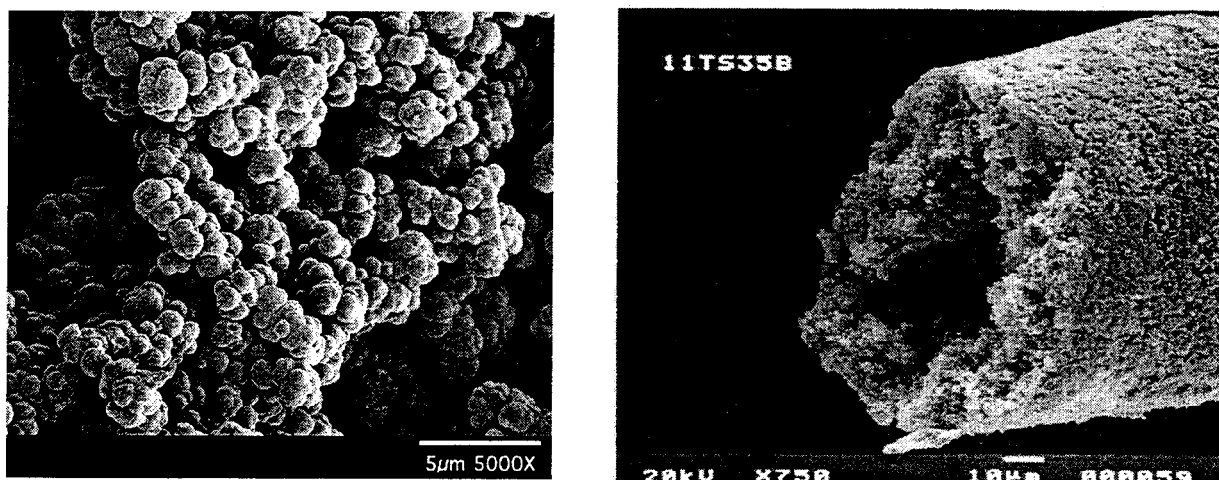


Figure 8: Acrylate-based porous polymer monolith.

We have examined a series of acrylate-based monoliths. To examine electronic and steric effects on separations, the acrylate was varied within the series to include ethyl, butyl, hexyl, dodecyl, t-butyl, tetrahydrofurfuryl (THF), and ethylene glycol phenyl ether (EGPE) acrylates.¹⁶ Increasing alkyl chain length from ethyl to dodecyl resulted in decreased zeta potentials, as we expected (Table 1). Similarly, incorporation of bulky acrylates (t-butyl, THF, EGPE) decreased zeta potentials. These results are presumably indicative of the screening effect of long-chain and bulky substituents.

Monolithic polymer frits

The ease of positioning and adhering to substrate of acrylate-based monoliths makes these materials promising for use as frit materials. Currently, fused silica frits are prepared in each capillary prior to packing with inorganic or organic particles. A small amount of nonporous silica (3.5 μ m) is packed into the bottom of each capillary and fused with a butane torch. These silica frits vary widely in reliability, with porosity and adhesion to the substrate varying with the amount and density of silica packed into the capillary, the water content in the silica, the silica particle size, the fusing temperature, and the fusing time; in short, frit making is commonly regarded as an art, with results varying widely from user to user. While it is difficult to prepare frits in capillaries, it is impossible to follow similar techniques on chips due to issues with geometry and materials incompatibility. Instead, complex mechanical stays such as multiple, closely placed columns or decreased channel depth are currently fabricated into the chip design. This complicates the chip design and can result in problems with flow patterns of the eluent. One common alternative to this method produces frits using sol-gel chemistry,²⁰ but this method, while perhaps more reliable than fused silica, is time consuming and probably inapplicable to chips. Another more recent advance reports the use of methacrylate-based polymers polymerized in situ to form frits;²² however, the monomers chosen for that process require at least 1h to polymerize.

While we have conducted most of our experiments using fused silica frits, we have found that the acrylate-based polymers make suitable substitutes for fused silica frits in our applications. The formulation used for the frits contained 10% hexyl acrylate (see Table 1) and was chosen for its pore size of 700 nm, as measured by Hg porosimetry.¹⁶ The acrylate monomer solution is introduced to a Teflon-coated capillary by capillary action until it reaches the required length. The capillary is then exposed to light at 365 nm for 5-15 minutes to induce polymerization, forming a frit. The placement of the frit is more easily controlled in a polyimide-coated capillary where a window is burned through the coating which otherwise acts as a mask. Upon exposure to 365 nm light, only the

monomer in the window is polymerized and has well-defined edges. We have measured zeta potentials of 3 μ m nonporous silica packed columns with fused silica and polymer monolith frits; no significant difference in zeta potentials was observed.

Conclusions

Streaming current measurements provide a rapid, reliable method of zeta potential determination, eliminating the need for porosity and tortuosity measurements. Problems with double layer thickness and electrode polarization can be minimized by careful selection of buffer. Acrylate-based polymer monoliths can be carefully chosen to obtain desired zeta potential for separations and/or electrokinetic pumping. Acrylate-based polymer monoliths can also be used as frits for particle-based packing materials.

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